NAREL Standard Operating Procedure
For
Actinides in Environmental Matrices
by Extraction Chromatography

Effective July 31, 2011

AM/SOP-1

National Air and Radiation Environmental Laboratory
Office of Radiation and Indoor Air
540 S. Morris Avenue
Montgomery, Alabama 36115
1-334-270-3400

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APPROVALS:

Shane Knockemus
Responsible Official, CERLS — Date: 7/20/11

Robert Lowry
Counting Room Manager, CERLS — Date: 7-22-11

Keith D. McCroan, PhD
Quality Assurance Officer, CERLS — Date: 7/25/11

John G. Griggs, PhD
Director, CERLS — Date: 7/20/11

Ananias Perry
Document Control Officer, NAREL — Date: 7/27/11

Mary F. Wisdom
Quality Assurance Manager, NAREL — Date: 7-20-11

Ronald G. Fraass
Director, NAREL — Date: 7/21/11

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1.0 PURPOSE

1.1 This standard operating procedure (SOP) describes a method for radiochemical analysis of actinides (americium, curium, neptunium, plutonium, thorium, and uranium) using extraction chromatography for the chemical separation of the analytes from a variety of environmental matrices, followed by alpha-particle spectrometry of the prepared source.

2.0 SCOPE AND APPLICATION

2.1 This method is applicable for the measurement of ^{241}Am, ^{238}Pu, ^{239}Pu, ^{227}Th, ^{228}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, and ^{238}U, (and ^{237}Np and $^{243/244}$Cm if desired) in a variety of environmental matrices, including water, soil, vegetation, air filters, and tissue.

2.2 The detection and quantification capabilities of this method are functions of sample size, interferences, instrument backgrounds, counting efficiency, and counting time. The actual minimum detectable activity (MDA) for each sample may be different based on any of these variables. For clean water samples, using a 1 L sample and a 1000 minute count time, an MDA of 0.1 pCi/L for ^{241}Am, ^{238}Pu, ^{239}Pu, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, and ^{238}U is usual. An MDA of 0.2 pCi/L for ^{227}Th and of 0.15 pCi/L for ^{228}Th is usual. For soil samples, using a 0.5 g aliquant and a 1000 minute count, an MDA of 0.2 pCi/g is generally obtainable for ^{241}Am, ^{238}Pu, ^{239}Pu, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, and ^{238}U. An MDA of 0.35 pCi/g for ^{227}Th, and of 0.3 pCi/g for ^{228}Th is obtainable.

2.3 Summary of Method

2.3.1 This procedure involves the use of a tandem arrangement of the TEVA™ and TRU columns or resin cartridges (available from Eichrom Technologies) containing extraction chromatographic resins, which effectively separate and isolate Am, Pu, Th, U and Np from a variety of environmental matrices. The columns are stacked so that the effluent from the TEVA resin column flows into the TRU resin column. The oxidation states of the elements of interest in the load solution are as follows: Am^{+3}, Np^{+4}, Pu^{+3}, Th^{+4}, and U^{+6}. Any Th or Np present in the sample will be retained on the TEVA resin, while any Am (and/or Cm), Pu, or U will pass through the TEVA resin column and be sorbed onto the TRU resin column.

2.3.2 The tandem column arrangement will then be separated and the elements of interest will be selectively eluted. The elements of interest will then be coprecipitated as a fluoride, and radioassayed by alpha-particle spectrometry.

2.3.3 If there is an analyte that is not requested for analysis there are steps within the procedure that can be altered to accommodate this without affecting the result of the other analyses. For example, if Th analysis is not requested, the use of the TEVA column is still necessary, but the elution, purification, and co-precipitation of Th is no longer necessary. Also, if U analysis is requested but Am and/or Pu is not, then the volume of solutions used to elute Am and Pu can be decreased without affecting the quality of the U analysis. Other scenarios do exist, such as omitting certain oxidation/reduction steps when only uranium is being analyzed.

2.4 Interferences

2.4.1 The ^{234}Th tracer, if not prepared properly, could potentially contain uranium. Before the ^{234}Th tracer is used it should be verified that there is no substantial uranium contamination which would lead to interferences in isotopic uranium analysis.

2.4.2 Actinides with unresolvable alpha energies such as ^{241}Am and ^{238}Pu, ^{237}Np and ^{234}U, ^{232}U and ^{228}Th, ^{228}Th and ^{241}Am, ^{232}U and ^{243}Am, and ^{228}Th and ^{238}Pu must be chemically separated to enable a reliable measurement. This method separates all of these isotopes effectively.

2.4.3 The presence of Fe^{+3} can interfere with the retention of the actinides on the resin. Any Fe^{+3} that is present in the sample must be reduced to Fe^{+2} with the addition of ascorbic acid so that it will not interfere with desired chemical reactions.

2.4.4 The presence of certain matrix constituents commonly associated with environmental samples, such as phosphates, sulfates, and oxalates, can cause interferences. The addition of Al^{+3} effectively complexes such ions so that they do not interfere with the analysis. In fact, the presence of Al^{+3} actually increases the retention factor of Am to the TRU column. There may be instances when increasing the Al^{+3} concentration in the nitric acid + aluminum nitrate load solution can be beneficial to radiochemical separation and recovery. If a higher concentration of Al^{+3} is needed, increase the amount of aluminum nitrate added in the preparation of the reagent in section 6.20. To achieve a 1 M concentration of aluminum nitrate, dissolve 376 g of aluminum nitrate nonahydrate in the same volume of other reagents listed.

2.4.5 Neptunium and americium can not be run sequentially. Each must be analyzed using a separate aliquant. The tracer used for Am analysis is ^{243}Am. The tracer used for Np analysis is ^{239}Np, which is in equilibrium with ^{243}Am. The ^{239}Np yield is determined by beta counting. In order to achieve acceptable counting statistics the amount of ^{239}Np added is equivalent to ~50 dpm of ^{243}Am.

3.0 DEFINITIONS

3.1 **assay batch** - a set of test sources prepared by one analyst at the same time, following one analytical method, and delivered to the nuclear counting laboratory for the same nuclear counting procedure.

3.2 **carrier** - a quantity of nonradioactive or nonlabeled material of the same chemical composition as its corresponding radioactive or labeled counterpart. When mixed with the corresponding radioactive labeled material, so as to form a chemically inseparable mixture, the carrier permits chemical (and some physical) manipulation of the mixture with less label or radioactivity loss than would be true for the undiluted label or radioactive material.

3.3 **Center for Environmental Radioanalytical Laboratory Science (CERLS)** - the Center at NAREL responsible for analyzing samples for radioactive constituents and hazardous chemicals; formerly the Monitoring and Analytical Services Branch (MASB).

3.4 **control chart** - a graph for monitoring the outputs of a process, such as an analytical measurement process, for the purpose of detecting conditions or trends adverse to quality.

3.5 **laboratory control sample (LCS)** - an artificial sample generated by the analyst in the laboratory and spiked with a known amount of one or more analytes. After being spiked, the LCS is prepared and analyzed in the same manner as a normal sample, and the result of the measurement is compared to the known amount of analyte added to assess the bias of the measurement process.

3.6 **laboratory information management system (LIMS)** - a database and software system used to manage radioanalytical data, monitor work processes, and produce reports.

3.7 **material safety data sheet (MSDS)** - a document that contains information on the potential health effects of exposure to chemicals or other potentially dangerous substances, and on safe working procedures workers should adhere to when handling chemical products.

3.8 **method blank** - an artificial sample generated by the analyst in the laboratory, which is as free as possible of the analyte of interest. The method blank is prepared and analyzed in the same manner as a normal sample and alongside real samples, so that the result of the measurement may be used to assess low-level bias in the measurement process, such as that caused by contamination of reagents, as well as cross-contamination of samples.

3.9 **method detection limit (MDL)** - A statistical analysis of a series of analytical data points to determine the concentration at which an analyte is able to be determined by a given method.

3.10 **minimum detectable activity (MDA)** - the minimum activity of analyte in a laboratory sample that guarantees a specified high probability of detection, usually 95 %.

3.11 **National Air and Radiation Environmental Laboratory (NAREL)** - the U.S. Environmental Protection Agency (EPA) Office of Radiation and Indoor Air's (ORIA) laboratory located in Montgomery AL.

3.12 **National Institute of Standards and Technology (NIST)** - the national standards body for the United States and a member organization of the International Organization for Standardization (ISO), formerly the National Bureau of Standards (NBS).

3.13 **NIST traceability** - Reference standards that are used in a radiochemical laboratory shall be obtained from the National Institute of Standards and Technology (NIST), or suppliers who participate in supplying NIST standards or NIST traceable radionuclides. Any reference standards purchased outside the United States shall be traceable back to each country's national standards laboratory. Commercial suppliers of reference standards shall conform to ANSI N42.22 to assure the quality of their products.

3.14 **Quality Assurance (QA) Manager** - the person with primary responsibility for overseeing NAREL's quality system.

3.15 **R value** - the ratio of observed activity divided by the actual amount of added activity, a measure of recovery.

3.16 **Radiochemistry Data Coordinator (RDC) –** person in CERLS who reviews analytical results, monitors the progress of analytical projects, and prepares data reports for clients.

3.17 **radiotracer (tracer)** - a radioactive isotope of the analyte, or of a chemically similar element, a measured amount of which is added to each test portion to measure the chemical yield.

3.18 **replicate sample (duplicate)** - an aliquant taken from one sample at the same time another aliquant is taken for normal preparation and analysis. Both aliquants are prepared and analyzed in the same manner. The analytical result for the second aliquant is compared to the result of the first aliquant to assess the precision of the measurement process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is greater.

3.19 **Safety, Health and Environmental Manager (SHEM)** - the person with primary responsibility for overseeing NAREL's Health and Safety Program.

3.20 **standard operating procedure (SOP)** - a document that describes in detail the steps for performing a routine task.

4.0 ROLES AND RESPONSIBILITIES

4.1 Unless otherwise noted, the radiochemist is responsible for performing all steps of this procedure. These responsibilities include grouping samples into QC batches, performing chemical separations and recording all data in laboratory notebooks.

4.2 Personnel in the Nuclear Counting Laboratory calibrate and maintain alpha-particle spectrometers, use them to analyze prepared samples, and perform the first review of analytical results.

4.3 The NAREL Radiochemistry Data Coordinator (RDC) performs a second review of each analysis performed using this method.

4.4 The NAREL QA Chemist is responsible for preparing ^{230}Th, ^{239}Pu, ^{241}Am, and ^{238}U spiking solutions.

5.0 EQUIPMENT AND SUPPLIES

5.1 Assorted glassware.

5.2 Membrane filters, 25 mm diameter, 0.1 µm - 0.2 µm pore size.

5.3 Suction filter apparatus for 25 mm membrane filters.

5.4 Stainless steel planchets, 32 mm diameter.

5.5 Petri dishes.

5.6 Tweezers.

5.7 Alpha spectrometric system consisting of multichannel analyzer, biasing electronics, printer, silicon surface barrier detectors, vacuum pump, and chamber.

5.8 Calibrated analytical balance, readability 0.1 mg or less.

5.9 Calibrated top-loading balance.

5.10 Hot plates.

5.11 Calibrated Eppendorf® auto pipets, assorted volumes.

5.12 Vacuum box (available from Eichrom Technologies).

6.0 REAGENTS AND STANDARDS

6.1 Reagent grade chemicals (or better) shall be used in all tests.

6.2 Reagent water in this method is laboratory de-ionized water which is treated by a point of use filtration system to ≥18.0 MΩ·cm resistivity (see the *De-ionized Water System* section in the *Equipment* chapter of the *NAREL Radiochemistry Quality Assurance Manual*) which is equivalent to ASTM Type 1, and shall be interference free. Analysis of a method blank must verify that the water is free from interferences.

6.3 Aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$, [CAS# 7784-27-2].

6.4 Ammonium hydrogen phosphate, $(NH_4)_2HPO_4$, [CAS# 7783-28-0].

6.4.1 Ammonium hydrogen phosphate, (3.2 M): Dissolve 104 g of $(NH_4)_2HPO_4$ in 200 mL of water, heat gently to dissolve, and dilute to 250 mL with deionized water.

6.5 Ammonium hydroxide, NH_4OH, (concentrated), [CAS# 1336-21-6].

6.6 Ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$, [CAS# 6009-70-7].

6.6.1 Ammonium oxalate (0.1 M): Add 14.2 g of ammonium oxalate to 900 mL of deionized water and dilute to 1 L with deionized water.

6.7 Ascorbic acid, powder, $C_6H_8O_6$, [CAS# 50-81-7].

6.8 Calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$, [CAS# 13477-34-4].

6.8.1 Calcium nitrate, (1.25 M): Dissolve 73.8 g of $Ca(NO_3)_2 \cdot 4H_2O$ in 100 mL of water and dilute to 250 mL with deionized water.

6.9 Cerium (III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$, [CAS# 10294-41-4].

6.10 Cerium +3 carrier: Dissolve 0.155 g cerium (III) nitrate hexahydrate in 50 mL of deionized water and dilute to 100 mL (0.5 mg/mL Ce^{+3}).

6.11 Denatured alcohol solution or equivalent, [CAS# 141-78-6].

6.12 Ferrous sulfamate, $Fe(NH_2SO_3)_2$, [CAS# 14017-39-1], (0.6 M): Add 57 g of sulfamic acid to 150 mL of deionized water, heat to 70 °C, add 7 g of iron powder in small increments until dissolved. Filter, transfer to a flask and dilute to 200 mL with deionized water. Prepare fresh weekly or purchase from Strem Chemical Co, (1-800-647-8736), catalog # 93-2638 Iron (II) sulfamate 25-30 % aqueous solution.

6.13 Hydrochloric acid, HCl, (concentrated, 12 M), [CAS# 7647-01-0].

6.13.1 Hydrochloric acid (6 M): Add 500 mL of concentrated HCl to 400 mL of deionized water and dilute to 1 L with deionized water.

6.13.2 Hydrochloric acid (4 M): Add 333 mL of concentrated HCl to 500 mL of deionized water and dilute to 1 L with deionized water.

6.13.3 Hydrochloric acid (1 M): Add 83 mL of concentrated HCl to 900 mL of deionized water and dilute to 1 L with deionized water.

6.13.4 Hydrochloric acid (0.1M): Add 8.3 mL of concentrated HCl to 900 mL of deionized water and dilute to 1 L with deionized water.

6.14 Hydrochloric acid (1 M) + oxalic acid (0.1 M) solution: Dissolve 12.6 g of oxalic acid in 900 mL of 1 M HCl and dilute to 1 L with 1 M HCl.

6.15 Hydrochloric acid (0.1 M) + hydrofluoric acid (0.05 M) + titanium chloride (0.03 M). Add 15 mL of 20 % titanium chloride per 500 mL of 0.1 M HCl and 0.05 M hydrofluoric acid. Prepare fresh within 30 minutes of intended use.

6.16 Hydrofluoric acid, HF, (concentrated, 29 M), [CAS# 7664-39-3].

6.16.1 Hydrofluoric acid (3 M): Add 52 mL of concentrated HF to 400 mL of deionized water and dilute to 500 mL with deionized water.

6.17 Iron, powder, Fe, [CAS# 7439-89-6].

6.18 Isopropyl alcohol, C_3H_7OH, (95 %), [CAS# 67-63-0].

6.19 Nitric acid, HNO_3, (concentrated, 16 M), [CAS# 7697-37-2].

6.19.1 Nitric acid (2.5 M): Add 156 mL of concentrated HNO_3 to 800 mL of deionized water and dilute to 1 L with deionized water.

6.20 Nitric acid (2.5 M) + aluminum nitrate (0.5 M) solution: Add 188 g of aluminum nitrate to 500 mL of deionized water, mix to dissolve, add 156 mL of concentrated HNO_3, and dilute to 1 L with deionized water.

6.21 Nitric acid (2.5 M) + sodium nitrite (0.1 M) solution: Dissolve 0.35 g of sodium nitrite in 50 mL of 2.5 M HNO_3. Prepare fresh solution daily.

6.22 Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$, (0.1 M) [CAS# 6153-56-6].

6.23 Perchloric acid, $HClO_4$, (concentrated) [CAS# 7601-90-3].

6.24 Phenolphthalein, $C_{20}H_{14}O_4$, [CAS# 77-09-8].

6.24.1 Phenolphthalein solution: Dissolve 1 g of phenolphthalein in 100 mL of 95 % isopropyl alcohol.

6.25 Sodium nitrite, $NaNO_2$, [CAS#: 7632-00-0].

6.26 Sulfamic acid, NH_2SO_3H, [CAS# 5329-14-6].

6.27 TEVA Resin prepacked column, or resin cartridge (available from Eichrom Technologies).

6.28 Titanium (III) chloride, $TiCl_3$, (10-15 % in hydrochloric acid) [CAS# 7705-07-9]. Replace within six months after opening. Store in amber bottle away from direct sunlight.

6.29 Tracers, calibrated: ^{243}Am, ^{242}Pu, ^{234}Th, and ^{232}U. ^{243}Am, ^{242}Pu, and ^{232}U are alpha emitters; ^{234}Th is a beta emitter.

6.30 TRU Resin prepacked column, or resin cartridge (available from Eichrom Technologies).

6.31 Nickel foil [CAS# 7440-02-0].

7.0 SAFETY

7.1 All procedures performed at NAREL must be conducted following the requirements detailed in the *NAREL Chemical Hygiene Plan* and the *NAREL Radiation Safety Manual*. Safety precautions associated with handling of chemical reagents, solutions, and all samples are the primary responsibility of the analyst. Any spills or accidents involving hazardous, corrosive, or toxic material must be immediately resolved.

7.2 All NAREL laboratory personnel are expected to use good laboratory practices. Most of the safety training is provided by the SHEM officer. The analyst is expected to comply with all directives given by the SHEM officer, and must take necessary precautions to prevent exposure or injury to both self and co-workers.

7.3 Unnecessary or prolonged exposure to laboratory chemicals should be avoided.

7.4 Aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$, [CAS# 7784-27-2], is a strong oxidizer; contact with other material may cause fire. Harmful if swallowed or inhaled. Causes irritation to skin, eyes and respiratory tract. Inhalation may result in coughing and shortness of breath. Ingestion may cause gastroenteritis and abdominal pain. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Keep separate from combustible, organic, or any other readily oxidizable materials. Store in a tightly closed container.

7.5 Ammonium hydrogen phosphate (ammonium phosphate dibasic), $(NH_4)_2HPO_4$, [CAS# 7783-28-0], causes irritation to skin, eyes and respiratory tract, and is harmful if swallowed or inhaled. Inhalation may result in coughing and shortness of breath. Ingestion may result in nausea, vomiting and diarrhea. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Store in a tightly closed container.

7.6 Ammonium hydroxide, NH_4OH, (concentrated), [CAS# 1336-21-6], is a poison and corrosive; may be fatal if swallowed or inhaled. Mist and vapor cause burns to every area of contact. Vapors and mists cause irritation to the respiratory tract; higher concentrations

can cause burns, pulmonary edema and death. Toxic: ingestion may cause corrosion to the esophagus and stomach with perforation and peritonitis; 3-4 mL may be fatal. Contact with skin causes irritation and burns. Contact with eyes by vapors causes irritation; splashes cause severe pain, eye damage, and permanent blindness. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Store in a tightly closed container; keep away from heat and direct sunlight.

7.7 Ammonium oxalate, $[(NH_4)_2C_2O_4 \cdot H_2O]$, [CAS# 6009-70-7], is poisonous and may be fatal if inhaled or ingested. Contact with skin or eyes can cause severe irritation and pain and may cause burns. Ammonium oxalate must be kept in a tightly closed container and stored in a dry, ventilated area, away from incompatible substances such as strong acids. Wash hands thoroughly after use.

7.8 Ascorbic acid, powder, $C_6H_8O_6$, [CAS# 50-81-7], is relatively non-hazardous but may cause mild irritation to the respiratory tract if inhaled, and mild irritation to skin and eyes upon contact. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use with adequate ventilation. Store in a tightly closed container; keep away from heat.

7.9 Calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$, [CAS# 13477-34-4], is a strong oxidizer; contact with other material may cause fire. Causes irritation to skin, eyes and respiratory tract. Harmful if swallowed or inhaled. Inhalation may result in coughing and shortness of breath, ingestion may result in nausea, vomiting and diarrhea. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Keep separate from incompatibles, combustibles, organic or other readily oxidizable materials. Store in a tightly closed container.

7.10 Cerium (III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$, [CAS# 10294-41-4], is a strong oxidizer; contact with other material may cause fire. Causes eye and skin irritation; may be harmful if absorbed through the skin. May cause respiratory tract irritation; may be harmful if inhaled. May cause irritation of the digestive tract. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Keep separate from incompatibles, combustibles, or other readily oxidizable materials. Hygroscopic. Store in a tightly closed container.

7.11 Ethyl alcohol (ethanol), C_2H_5OH, [CAS# 64-17-5], is flammable as a liquid and as a vapor. Inhalation may cause drowsiness and irritation to the respiratory tract. Avoid skin and eye contact by using appropriate protective clothing. Use only in a well-ventilated area away from open flames and ignition sources. Store in containers approved for ethyl alcohol.

7.12 Ferrous sulfamate, $Fe(NH_2SO_3)_2$, is irritating to skin and eyes; may be irritating to the respiratory tract and may be harmful if swallowed. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use with adequate ventilation. Store in a tightly closed container; keep away from heat and direct sunlight.

7.13 Hydrochloric acid, HCl, [CAS# 7647-01-0], is harmful if swallowed, inhaled, or ingested. It can cause serious damage to eyes and skin. Ingestion can cause burns around the mouth, throat, and esophagus with irritation and pain. Hydrochloric acid causes chemical burns following contact with skin and eyes. Inhalation can cause toxic effects and may be fatal. Use hydrochloric acid only with adequate ventilation and appropriate protective clothing. Always release caps slowly to ensure slow dissipation of vapors. Store concentrated hydrochloric acid in the original container, securely sealed, in a cool, dry, well-ventilated area, away from alkaline materials, galvanized steel, and zinc. Avoid strong bases. Do not discharge into sewer or waterways.

7.14 Hydrofluoric acid, HF, [CAS# 7664-39-3], is a highly reactive chemical. It must be stored in plastic containers, and away from light, heat, and strong bases. Hydrofluoric acid is highly destructive to tissue and may be fatal if inhaled, swallowed, or absorbed through the skin. Hydrofluoric acid should be used only by persons trained and familiar with appropriate safety precautions.

7.15 Iron, powder, Fe, [CAS# 7439-89-6], may cause irritation to eyes and the respiratory tract. Avoid inhalation and contact with eyes by using appropriate protective clothing and equipment. Use with adequate ventilation. Avoid dust formation and ignition sources. Store in a tightly closed container.

7.16 Isopropyl alcohol (isopropanol), C_3H_7OH, [CAS# 67-63-0], is flammable and may be violently or explosively reactive. Ingestion can cause gastritis, nausea, vomiting, and diarrhea, as well as nervous system symptoms and lung damage. Isopropanol causes eye and skin irritation on exposure. Inhalation of vapors can cause drowsiness, dizziness, headaches, muscle weakness, seizures, and unconsciousness. Containers, even those that have been emptied, can contain explosive vapors. Unopened containers received from the manufacturer are safe to store for 18 months. Opened containers should not be stored for more than 12 months. Avoid all personal contact and use in a well ventilated area. Do not use aluminum or galvanized containers. Store in the original container away from heat and flame sources, and away from strong acids, acid anhydrides, and oxidizing agents. Do not discharge into sewers or waterways.

7.17 Nitric acid, HNO_3, [CAS# 7697-37-2], is poisonous, reactive, and a strong oxidizer. Contact with other materials may cause fire. It can cause burns to body tissues and may be fatal if ingested or inhaled. Vapors are irritating to eyes and mucous membranes. Use only with adequate ventilation and proper protective clothing and gloves. Nitric acid is incompatible with most substances, especially strong bases, metallic powders, carbides, and combustible organics. Store away from light and heat.

7.18 Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$, [CAS# 6153-56-6], is a poison and corrosive; may be fatal if swallowed or inhaled. Causes severe irritation and burns to skin, eyes, and respiratory tract. Harmful if inhaled or absorbed through skin. May cause kidney damage. Harmful if inhaled: can cause severe irritation and burns of nose, throat and respiratory tract. Toxic: ingestion may cause burns, nausea, severe gastroenteritis and vomiting, shock and convulsions. May cause renal damage; estimated fatal dose is 5-15 grams. Contact with skin can cause severe irritation and burns; may be absorbed through skin. Contact with eyes can cause severe irritation and may produce corrosive effects. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Store in a tightly closed container; keep away from heat and incompatibilities.

7.19 Perchloric acid, $HClO_4$, [CAS# 7601-90-3], is a strong oxidizer. It is explosive in the presence of heat, oxidizing materials, and organic materials. Contact with other material may cause a fire. It is corrosive and hygroscopic. Perchloric acid is severely corrosive to eyes and skin. It is toxic if inhaled or ingested and may cause burns to mouth, throat, and stomach. Perchloric acid may cause severe irritation of the respiratory tract if inhaled. Do not store perchloric acid near combustible materials; it increases the risk of fire and may aid combustion. Store in a cool, dry place in a tightly closed container and use only with adequate ventilation. Use perchloric acid only in a hood that is used exclusively for perchloric acid. Keep the hood clean and do not allow buildup of dried perchloric crystals in the hood. Solid crystals may undergo spontaneous and explosive decomposition. Always wear eye, skin, and clothing protection when using perchloric acid. Perchloric acid should be used only by persons trained and familiar with appropriate safety precautions.

7.20 Phenolphthalein, $C_{20}H_{14}O_4$, [CAS# 77-09-8], is harmful if swallowed, a suspect cancer hazard. Nuisance dust; inhalation may cause coughing and sneezing. May cause slight irritation to eyes upon contact. Cathartic, even in small amounts (30-100 mg); ingestion/absorption may cause purging, collapse, blood pressure drop, or itching/ulcerous skin rash. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Store in a tightly closed container.

7.21 Sodium nitrite, $NaNO_2$, [CAS#: 7632-00-0], is a strong oxidizer; contact with other material may cause fire. Heat, shock, or contact with other material may cause fire or explosive decomposition. Harmful if swallowed, inhaled or absorbed through skin. Causes irritation to skin, eyes and respiratory tract. Toxic: inhalation causes irritation to the respiratory tract and systemic poisoning with symptoms paralleling indigestion. Ingestion can irritate the mouth, esophagus, stomach, etc.; excessive amounts affect the blood and blood vessels (estimated lethal dose 1-2 grams). Contact with skin and eyes causes irritation, redness, and pain; may be absorbed through skin, causing systemic poisoning. Avoid contact with skin and eyes by using appropriate protective clothing and equipment. Use only with adequate ventilation. Keep separate from incompatibles, combustibles, organic or any other readily oxidizable materials. Store in a tightly closed container away from heat.

7.22 Sulfamic acid, NH_2SO_3H, [CAS# 5329-14-6], is corrosive to eyes and skin and may cause burns to mouth, throat, and stomach. Use only with adequate ventilation. Wear appropriate gloves and eye protection when using sulfamic acid. Store in tightly closed container in a cool, well-ventilated area. The generation of waste should be avoided or minimized wherever possible. Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains, and sewers.

7.23 Titanium chloride, $TiCl_3$, [CAS# 7705-07-9], is a flammable solid and can cause severe eye and skin burns. Replace within six months after opening. Store in amber bottle away from direct sunlight.

7.24 Material safety data sheets (MSDS) are available to all personnel involved in chemical analysis. It is the responsibility of each analyst to be familiar with chemicals used during an analysis.

7.25 Refer to the *NAREL Chemical Hygiene Plan* for verification of appropriate safety and health practices.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Soil samples can be shipped to the laboratory in either plastic or glass containers. No preservation is required.

8.2 Water samples can be shipped in either plastic or glass containers. Nitric acid should be added to the sample in the field to bring the pH to less than 2. Upon receipt of the samples, NAREL staff checks the pH of each water sample for actinides analysis, and adjusts the pH as necessary.

8.3 Special handling such as refrigeration or freezing may be required for samples of other matrices such as animal tissue or vegetation.

8.4 Samples for actinides analysis do not require refrigeration during storage.

9.0 CALIBRATION AND STANDARDIZATION

9.1 A detailed procedure for preparing the ^{234}Th tracer is presented in *NAREL Standard Operating Procedure for Preparing Thorium-234 Tracer Solutions* (AMS/SOP-4).

9.2 A detailed procedure for preparing the ^{232}U tracer is presented in *NAREL Standard Operating Procedure for Preparation of Self-Cleaning U-232 Tracer Solution* (AMS/SOP-6).

9.3 All fixed volume pipets used must be calibrated and checked in accordance with the *NAREL Standard Operating Procedure for Calibration, Use, and Maintenance of Pipets* (SE/SOP-4).

9.4 All balances used must be calibrated and checked in accordance with the *NAREL Standard Operating Procedure for Calibration of Balances* (SE/SOP-1).

9.5 All alpha spectrometers must be calibrated in accordance with the *NAREL Standard Operating Procedure for Calibration and Use of Alpha Spectrometers Using AlphaVision* (NC/SOP-8).

10.0 PROCEDURE

10.1 Sample Preparation:

10.1.1 Measure the appropriate aliquant of sample for analysis.

10.1.1.1 Since there is a limit to the total activity that can be placed in an alpha spectrometer chamber, samples for alpha-particle spectrometry should be analyzed first for gross alpha radiation if there is adequate sample available.

10.1.1.2 The aliquant size in grams ashed (gash) for solid samples for actinides (except thorium, which uses a beta-emitting tracer) can be computed as follows:

10.1.1.2.1 Subtract the alpha tracer activity in picocuries from 30 pCi.

10.1.1.2.2 Divide the difference by the gross alpha concentration in pCi/gash.

10.1.1.2.3 If the computed size is less than 0.25 gash, take an aliquant and perform a dilution to obtain the required amount.

10.1.1.3 The aliquant size in milliliters for water samples for actinides (except thorium, which uses a beta-emitting tracer) is computed as follows:

10.1.1.3.1 Subtract the alpha tracer activity in picocuries from 30 pCi.

10.1.1.3.2 Divide the difference by the gross alpha concentration in pCi/mL to determine the volume of the aliquant.

10.1.2 Add appropriate tracer(s).

10.1.2.1 The procedure to prepare the ^{234}Th tracer is documented in *NAREL Standard Operating Procedure for Preparing Thorium-234 Tracer Solutions* (AMS/SOP-4). The procedure for preparing ^{232}U tracer is presented in *NAREL Standard Operating Procedure for Preparation of Self-Cleaning U-232 Tracer Solution* (AMS/SOP-6). Other tracers are distributed to analysts by the NAREL QA Manager. Their preparation and validation are described in *NAREL Standard Operating Procedure*

for Preparing and Validating Radiochemical Tracers, Spiking Solutions, and Calibration Solutions (QA/SOP-4).

10.1.2.2 The activity of a ^{232}U, ^{242}Pu, ^{243}Am added to a sample should be at least 4 dpm to ensure that the uncertainty in the yield will be small. The activity should not be more than 8 dpm.

10.1.2.3 The ^{234}Th tracer activity should be 2000 - 5000 cpm per sample.

10.1.2.4 The ^{239}Np tracer (beta-emitter) activity should be equivalent to ~50 dpm of ^{243}Am.

10.1.2.5 NOTE: Standard procedure requires that appropriate tracer(s) be added to each sample before digestion or other preparation steps are begun. In rare circumstances, the analyst may digest the solid sample aliquant before adding the tracer(s), bring the dissolved sample to a measured volume, remove a measured portion of the solution as a sample, and then add tracer(s). This can be done when the total sample alpha activity as indicated by the gross alpha result is high enough that a very small soil aliquant must be taken to keep sample activity with tracer below 30 pCi. Measurement of such a small aliquant, with associated large uncertainty, is avoided by the digestion and dilution procedure. Similarly, if a sample result indicates probable matrix interference, the analyst may use the digestion and dilution process to minimize matrix effect for the repeat preparation and analysis. In any case where this procedure is used, the analyst must document fully the reason for the deviation from the SOP in the logbook and on the assay batch form. The RDC is then responsible for describing the deviation and its rationale in the report to the client.

10.1.3 Preparation options:

10.1.3.1 Preparation technique for hotplate digestion of solid samples.

10.1.3.1.1 Weigh aliquant of solid sample (preferable ashed) into a Teflon beaker.

10.1.3.1.2 Wet the sample aliquant with a small amount of water or dilute HNO_3.

10.1.3.1.3 Add appropriate tracer(s).

10.1.3.1.4 Add 5 - 10 mL 16 M HNO_3.

10.1.3.1.5 Add 20 - 50 mL 29 M HF.

10.1.3.1.6 Place on hotplate at medium-hot setting. Evaporate to dryness.

10.1.3.1.7 Inspect the sample. If it appears silica remains then repeat HF treatment. If silica appears to be adequately removed from the sample, add ~5 mL 16 M HNO_3 and evaporate to dryness.

10.1.3.1.8 Add 5 - 10 mL 16 M HNO_3 and 5 - 10 mL 12 M HCl. Place beaker on hotplate to dissolve residue. Transfer dissolved sample from Teflon beaker to a labeled glass beaker. Rinse the Teflon beaker with HNO_3 and/or HCl, and combine with original sample.

10.1.3.1.9 Place beaker on hotplate. Evaporate to dryness. If the analyst determines that some organic material remains undigested in the sample, add 5 - 10 mL 16 M HNO_3 and 5 - 10 mL 12 M $HClO_4$ and evaporate to dryness.

10.1.3.1.10 Add 5 - 10 mL 16 M HNO_3. Evaporate to dryness.

10.1.3.1.11 Dissolve residue in 10 - 20 mL of load solution. Proceed to section 10.2.

10.1.3.2 Preparation technique for digestion of water samples.

10.1.3.2.1 Measure sample aliquant.

10.1.3.2.2 Add appropriate tracers.

10.1.3.2.3 Add 5 - 10 mL 16 M HNO_3 and 5 - 10 mL 12 M HCl. Place sample on hotplate and evaporate to dryness.

10.1.3.2.3.1 If it appears that the sample contains siliceous material as the sample volume decreases during evaporation, treatment with HF may be applicable. If so, transfer the sample to a Teflon beaker, add 20 - 50 mL 29 M HF, and continue the digestion of the sample as described beginning with step 10.1.3.1.6.

10.1.3.2.3.2 If it appears that the sample contains organic material, treatment with $HClO_4$ may be applicable. If so, see step 10.1.3.1.9.

10.1.3.2.4 Add 5 - 10 mL 16 M HNO_3. Evaporate to dryness.

10.1.3.2.5 Dissolve residue in 10 - 20 mL of load solution. Proceed to section 10.2.

10.1.3.3 Preparation techniques for the microwave assisted acid digestion of solid and semi-solid samples (soils, oils, or tissues) are described in the *NAREL Standard Operating Procedure for Microwave Digestion of Samples for Actinide, Strontium, Radium, and Alpha/Beta Analyses* (AMS/SOP-7).

10.1.3.4 Calcium phosphate precipitation option for water samples. This option offers an efficient means for water sample preparation when a large sample volume (0.5 - 3 L) is required to achieve required detection limits.

10.1.3.4.1 Add 0.5 mL of 1.25 M $Ca(NO_3)_2$ to each sample.

10.1.3.4.2 Place the sample on a hotplate at a high setting. Heat the sample to a boil. Once the sample boils, lower the setting of the hotplate to a low-medium setting.

10.1.3.4.3 Add ~3 drops of phenolphthalein indicator and 0.2 mL of 3.2 M $(NH_4)_2HPO_4$.

10.1.3.4.4 Slowly add enough NH_4OH to reach the phenolphthalein endpoint (pink) and begin the formation of the $Ca_3(PO_4)_2$ precipitate. Add a stir bar to the beaker, place the beaker

back on the hotplate, and allow to heat with stirring for at least 30 minutes.

10.1.3.4.5 Remove the stir bar, and allow the precipitate time to settle (30 minutes to 2 hours) or centrifuge, so that the solution can be decanted.

10.1.3.4.6 Decant the supernatant and discard as waste.

10.1.3.4.7 Quantitatively transfer the precipitate to a centrifuge tube (either 50 mL or 250 mL tube), and spin at 2000 rpm for at least 2 minutes.

10.1.3.4.8 Wash the precipitate with an amount of deionized water approximately twice the volume of the precipitate. Mix well and centrifuge. Discard the supernatant.

10.1.3.4.9 If ammonia odor persists, repeat washing step.

10.1.3.4.10 Dissolve the precipitate in 3 - 5 mL of 16 M HNO_3, and transfer the solution to a beaker. Rinse the centrifuge tube with 2 - 3 mL of 16 M HNO_3 and combine with the solution in the beaker.

10.1.3.4.11 Place the beaker containing the sample on a hotplate on a medium setting and evaporate to dryness (do not bake).

10.1.3.4.12 The sample is now ready for radiochemical separation. Proceed to step 10.2.1.

10.2 Column or Cartridge Preparation:

10.2.1 For each sample to be analyzed, place one TEVA resin and one TRU resin column in a tandem arrangement so that the effluent from the TEVA column flows into the TRU column.

10.2.2 All draining steps in the procedure may make use of a vacuum box to speed up flow through the columns or cartridges. Generally the flow rate is set at 1 - 2 mL per minute.

10.2.3 Condition the columns with 5 mL of 2.5 M HNO_3. Allow them to drain. Discard the effluent.

10.3 Chemical Separation:

10.3.1 Dissolve the digested sample in 10 - 15 mL of the HNO_3 + $Al(NO_3)_3$ solution. Visually inspect the sample to make sure there are not any residual solids remaining in the sample before it is poured onto the column. Even a small amount of residual matter can clog the frit on the column, making it difficult for the sample to flow through the column at an acceptable rate. If residual solids are present, take the appropriate steps to remove them (ex. Filtering or centrifuging). Add 2 mL of ferrous sulfamate solution. Ferrous sulfamate reduces Pu^{+4} to Pu^{+3} to enable a clean Th/Pu separation. Ferrous sulfamate also reduces neptunium to Np^{+4}.

10.3.2 Add approximately 200 mg of ascorbic acid. Samples high in Fe^{+3} might require additional ascorbic acid. Swirl the sample to mix and allow the ascorbic acid to dissolve. Pour the sample solution into the reservoir on the top column of the tandem setup.

10.3.3 Rinse the beaker that contained the sample with 5 mL 2.5 M HNO_3 and 1 mL of ferrous sulfamate. Add to the reservoir with sample solution currently on the column. Allow the sample to drain through both columns. Discard the effluent.

10.3.4 Add 5 mL of 2.5 M HNO_3 to the reservoir on the top column, and allow it to drain. Discard the effluent.

10.3.5 Disconnect the two columns. From this point on the TEVA Resin and TRU resin columns will be run separately and simultaneously.

10.4 Purification and Elution of Thorium and Neptunium:

10.4.1 Rinse the TEVA column with 5 mL of 2.5 M HNO_3. Discard the effluent.

10.4.2 Place a clean 50 mL polypropylene centrifuge tube labeled with sample number and “Th” below the appropriate column/cartridge.

10.4.3 Add 15 - 20 mL of 6 M HCl to each reservoir to elute the Th from the column/cartridge. Collect the effluent.

10.4.4 Set solution containing the thorium strip aside for source preparation (step 10.6).

10.4.5 Place a clean 50 mL polypropylene centrifuge tube labeled with sample number and “Np” below the appropriate column/cartridge.

10.4.6 Add 15 - 20 mL of the Np strip solution (HCl + HF + $TiCl_3$). Collect the effluent.

10.4.7 Set solution containing the neptunium strip aside for source preparation (step 10.6.7).

10.4.8 Thorium and neptunium samples do not contain an alpha emitting tracer. For Th and Np samples a standard must be prepared for each assay batch taken to the Nuclear Counting Laboratory (NCL). The standard is prepared by adding an equal volume of tracer that was used with the samples into a 50 mL centrifuge tube or appropriate size beaker. Dilute the tracer to ~10-15 mL with 1 M HCl. Set aside until source preparation (section 10.6). The standard does not go through the radiochemical separation process. It is to be precipitated and filtered at the same time as the samples. The standard and samples are beta counted on proportional counters. The ratio of the sample to the standard counts is used to determine the radiochemical yield for Th and Np analysis.

10.5 Purification and Elution of Americium, Plutonium, and Uranium:

10.5.1 Rinse the TRU column with 5 mL of 2.5 M HNO_3. Discard the effluent.

10.5.2 Add 5 mL of HNO_3 + $NaNO_2$ to the column and allow it to drain through the column. Discard the effluent. This step changes the oxidation state of Pu from +3 to +4 to allow for separation of Am and Pu (Am remains at +3).

10.5.3 Add 5 mL of 2.5 M HNO_3 to the column to rinse out the $NaNO_2$. Discard the effluent.

10.5.4 Place a clean beaker or a 50 mL polypropylene centrifuge tube labeled with sample number and “Am” under each column/cartridge.

10.5.5 Add ~20 mL of 4 M HCl to each column to elute the americium. (Discard the effluent if not analyzing for americium).

10.5.6 Set the container with the americium strip aside for source preparation (step 10.6).

10.5.7 Place a clean beaker or 50 mL polypropylene centrifuge tube labeled with sample number and "Pu" under each column/cartridge.

10.5.8 Add ~15 mL of the HCl + $H_2C_2O_4$ solution to each column to elute the plutonium. Collect the effluent.

10.5.9 Set the container with the plutonium strip aside for source preparation (step 10.6.7).

10.5.10 Place a clean beaker or 50 mL polypropylene centrifuge tube labeled with sample number and "U" under each column.

10.5.11 Add ~20 mL of 0.1 M $(NH_4)_2C_2O_4$ to each column to elute the uranium. Collect the effluent.

10.5.12 Set the container with the uranium strip aside for source preparation (step 10.6.6).

10.5.13 If the sample is suspected of being unusually high in Polonium (PUUA samples) the Po must be removed. If there is any ^{210}Po in the sample it will conflict with the ^{232}U ROI and cause a high ^{232}U tracer recovery. Cut a piece of Nickel foil approximately 4-10 cm^2. Put the piece of Ni foil directly into the strip solution containing the U fraction. Place the sample in a warm water bath (below boiling) for 1-2 hours to enable any Po in the sample to plate out on the Ni foil. Remove the Ni foil and proceed to step 10.6.6.

10.6 Source Preparation:

10.6.1 Place the americium and thorium fractions on a hotplate at medium heat, and evaporate to near dryness.

10.6.2 Add 2 - 5 mL of 16 M HNO_3 and 3 - 10 mL of 12 M perchloric acid to each beaker. This treatment will oxidize any extractant that might have been stripped from the resin. The presence of extractant deposited on the membrane filter will retard sample resolution.

10.6.3 Evaporate to dryness.

10.6.4 Add 3 - 5 mL of 12 M HCl to each beaker. Evaporate to near dryness. Do not bake.

10.6.5 Add 10 - 15 mL of 1 M HCl to each beaker. If some extractant is visible in the sample then repeat the perchloric acid treatment.

10.6.6 Add 0.2 - 0.5 mL of $TiCl_3$ to uranium fractions only. The $TiCl_3$ reduces U^{+6} to U^{+4} to enable the uranium to be coprecipitated.

10.6.7 Add 50 - 100 µg of Ce^{+3} carrier (e.g., 0.1 - 0.2 mL of a 500 ppm Ce^{+3} solution) to all beakers (Am, Pu, Np, Th, and U).

10.6.8 Add 5 mL of 3 M HF to each beaker. Swirl gently to mix, and set aside for 30 minutes to precipitate.

10.6.9 Filter the solution through a 0.1 - 0.2 µm pore size membrane filter with the use of a microfiltration apparatus.

10.6.10 Rinse the filter chimney with 5 mL of deionized water.

10.6.11 Rinse the filter chimney with 5 mL of ethanol.

10.6.12 Prepare a source by mounting the filter containing the precipitate on a 32 mm stainless steel planchet fixed with double-sided tape or glue.

10.6.13 Beta-count the source to measure ^{234}Th or ^{239}Np recovery, if analyzing for either thorium or neptunium.

10.6.14 Submit the source to the nuclear counting laboratory for alpha-particle spectrometry.

10.6.15 NOTE: Samples analyzed for thorium must be counted by the fifth night after the separation step.

11.0 QUALITY CONTROL PROCEDURES

11.1 Reference standards used to provide tracers, spiking solutions, standards, or calibration sources must be obtained from the National Institute of Standards and Technology (NIST) or suppliers who participate in supplying NIST standards or NIST traceable radionuclides.

11.2 For each QC batch of up to 20 samples of the same matrix, the analyst must add the following quality control samples:

11.2.1 method blank.

11.2.2 laboratory control sample (LCS).

11.2.2.1 At least one analyte must be included in any LCS. For analytical methods that measure more than one analyte, it is not necessary to include every analyte in the LCS; however, each analyte that is included must be evaluated.

11.2.2.2 The activity of an analyte added to the LCS must be at least five times the normal expected minimum detectable activity (MDA) for that analyte and should be comparable to sample activities when sample activities in the batch are expected to be higher than five times the MDA. The spike level should be high enough to ensure that under expected measurement conditions, the relative standard counting uncertainty will not exceed 5 %.

11.2.3 replicate sample (duplicate).

11.3 Analysts are required to control chart results from blanks and laboratory control samples, and to observe the control charts for indicators of possible problems in the measurement system. LIMS software allows the analyst to input data points and to view and print the control charts.

11.4 See the *NAREL Radiochemistry Quality Assurance Manual* (QA/QAM-1) for acceptance criteria for QC samples, and equations for calculating values for quality indicators.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 All equations shown here represent *values* of quantities, not *numerical values*. To calculate with numerical values, either use coherent units (e.g., SI units) or include the appropriate unit-conversion factors in the equations.

12.2 *Chemical Yield:*

12.2.1 To calculate the chemical yield and associated standard uncertainty for an americium, plutonium, or uranium analysis, use the following equations.

$$Y = \frac{\frac{C_{ST}}{t_S} - \frac{C_{BT}}{t_B}}{\varepsilon \times c_T \times V_T \times D_T \times P_T} \quad (1)$$

$$u(Y) = \sqrt{\frac{\frac{C_{ST}+1}{t_S^2} + \frac{C_{BT}+1}{t_B^2} + \xi_{BT}^2}{\varepsilon^2 c_T^2 V_T^2 D_T^2 P_T^2} + Y^2\left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(c_T)}{c_T^2} + \frac{u^2(V_T)}{V_T^2} + \frac{u^2(P_T)}{P_T^2}\right)} \quad (2)$$

where

Y is the chemical yield,
C_{ST} is the gross (sample) count in the tracer ROI,
C_{BT} is the background count in the tracer ROI,
t_S is the length of the sample counting period (usually 1000 min or more),
t_B is the length of the background counting period (usually 3000 min),
ε is the alpha-particle detection efficiency,
c_T is the activity concentration of the tracer solution,
V_T is the volume of tracer solution added to the sample aliquant,
D_T is the decay factor for the tracer, which corrects for the decay of the tracer from its reference date and time through the counting period (see below),
P_T is the alpha-particle emission probability for the tracer ROI, and
ξ_{BT} is the additional uncertainty of the background correction due to background instability in the tracer ROI (expressed as a count rate)

12.2.2 The decay factor D_T in 12.2.1 is calculated as follows.

$$D_T = e^{-\lambda_T t_{DT}} \times \frac{\sinh(\lambda_T t_S / 2)}{\lambda_T t_S / 2} \quad (3)$$

where

λ_T is the decay constant for the tracer radionuclide and
t_{DT} is the elapsed time from the tracer reference date and time to the midpoint of the counting period

NOTE: It is acceptable to use the simpler equation $D_T = e^{-\lambda_T t_{DT}}$ instead of equation 3, because the omitted factor is nearly equal to 1 except in the case of very short-lived radionuclides or very long count times. The same type of simplification may be made to equation 14 below.

12.2.3 The chemical yield for a thorium analysis is measured using ^{234}Th, a beta-emitter, as a tracer. To calculate the yield and associated standard uncertainty for a thorium analysis, use the following equations.

$$Y = \frac{\frac{C_{S\beta}}{t_\beta} - R_{B\beta}}{\frac{C_{R\beta}}{t_\beta} - R_{B\beta}} \qquad \text{and} \qquad u(Y) = Y \times \sqrt{J \times \left(\frac{1}{C_{S\beta}} + \frac{1}{C_{R\beta}} \right)} \tag{4}$$

where

Y is the yield,
$C_{S\beta}$ is the gross beta count for the sample source,
$C_{R\beta}$ is the gross beta count for the reference source,
$R_{B\beta}$ is the beta background count rate,
t_β is the beta count time for the sample source and for the reference source,
J is the index of dispersion for the ^{234}Th+^{234m}Pa count distribution (see below)

12.2.4 Calculate the index of dispersion for the ^{234}Th+^{234m}Pa count distribution as follows.

$$J = 1 + \varepsilon_\beta \left(\frac{\mu_2'}{\mu_1'} - 1 \right) \tag{5}$$

where ε_β = 0.50 (assumed 50 % beta detection efficiency),

$$\mu_n' = p_{01} + 2^n p_{02} + \frac{\lambda_{Th}}{\lambda_{Pa} - \lambda_{Th}} p_{12}, \qquad \text{for } n = 1, 2, \tag{6}$$

$$p_{01} = \frac{\lambda_{Th}}{\lambda_{Pa} - \lambda_{Th}} (e^{-\lambda_{Th} t_\beta} - e^{-\lambda_{Pa} t_\beta}) \tag{7}$$

$$p_{02} = 1 + \frac{\lambda_{Th} e^{-\lambda_{Pa} t_\beta} - \lambda_{Pa} e^{-\lambda_{Th} t_\beta}}{\lambda_{Pa} - \lambda_{Th}} \tag{8}$$

$$p_{12} = 1 - e^{-\lambda_{Pa} t_\beta} \tag{9}$$

and

λ_{Th} is the radioactive decay constant for ^{234}Th,
λ_{Pa} is the radioactive decay constant for ^{234m}Pa, and
t_β is the beta count time for the test source and reference source

12.3 *Activity:*

12.3.1 For americium, plutonium, or uranium, use the following equations to calculate the volumic or massic activity of each analyte, and the associated uncertainty.

$$x = \frac{\frac{C_{SA}}{t_S} - \frac{C_{BA}}{t_B}}{\varepsilon \times V_A \times Y \times D_A \times P_A} = \frac{\frac{C_{SA}}{t_S} - \frac{C_{BA}}{t_B}}{\frac{C_{ST}}{t_S} - \frac{C_{BT}}{t_B}} \times \frac{c_T \times V_T \times D_T \times P_T}{V_A \times D_A \times P_A} \tag{10}$$

$$u(x) = \sqrt{\frac{\frac{C_{SA}+1}{t_S^2} + \frac{C_{BA}+1}{t_B^2} + \xi_{BA}^2}{\varepsilon^2 V_A^2 Y^2 D_A^2 P_A^2} + x^2\left(\left(\frac{u^2(Y)}{Y^2} - \frac{u^2(\varepsilon)}{\varepsilon^2}\right) + \frac{u^2(V_A)}{V_A^2} + \frac{u^2(P_A)}{P_A^2} + \varphi_S^2\right)} \quad (11)$$

where

x is the volumic or massic activity of the analyte,
C_{SA} is the gross (sample) count in the analyte ROI,
C_{BA} is the background count in the analyte ROI,
t_S is the length of the sample counting period,
t_B is the length of the background counting period,
ε is the alpha-particle detection efficiency,
Y is the chemical yield (equation 1),
V_A is the size of the sample aliquant (e.g., volume or mass),
D_A is the decay factor for the analyte, which corrects for decay of the analyte from the reference date and time through the counting period (see below),
P_A is the alpha-particle emission probability for the analyte ROI,
ξ_{BA} is the additional uncertainty of the background correction due to background instability in the analyte ROI (expressed as a count rate), and
φ_S is the relative standard uncertainty due to subsampling

If the aliquant size V_A is a mass, then

$$\varphi_S = \sqrt{\frac{(0.4\text{g/cm}^3)d^3}{m_S}}$$

where

d = 0.1 cm, and
m_S is the mass of sample dissolved

If the aliquant size is a volume or if it is 1 SAMP or 1 FILT, then $\varphi_S = 0$.
In all other cases φ_S is assumed by default to be 0.05.

12.3.2 For thorium isotopes, use the following equations to calculate the volumic or massic activity of each analyte, and the associated uncertainty.

$$x = \frac{\frac{C_{SA}}{t_S} - \frac{C_{BA}}{t_B}}{\varepsilon \times V_A \times Y \times D_A \times P_A} \quad (12)$$

$$u(x) = \sqrt{\frac{\frac{C_{SA}+1}{t_S^2} + \frac{C_{BA}+1}{t_B^2} + \xi_{BA}^2}{\varepsilon^2 V_A^2 Y^2 D_A^2 P_A^2} + x^2\left(\frac{u^2(Y)}{Y^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V_A)}{V_A^2} + \frac{u^2(P_A)}{P_A^2} + \varphi_S^2\right)} \quad (13)$$

12.3.3 The decay factor D_A in 11.3.1 and 11.3.2 is calculated as follows.

$$D_A = e^{-\lambda_A t_{DA}} \times \frac{\sinh(\lambda_A t_S/2)}{\lambda_A t_S/2} \quad (14)$$

where

λ_A is the decay constant for the analyte and
t_{DA} is the elapsed time from the reference date and time to the midpoint of the counting period ($t_{DA} = t_S / 2$ if the reference date and time equals the start of counting)

Equation 14 may also be simplified in the manner described in the note below Equation 3.

12.4 For all analyses and isotopes, use the following equations to calculate the critical net count rate and the critical value of the massic or volumic activity.

$$S_C = \frac{z_{0.95}^2}{2t_B} + z_{0.95}\sqrt{\frac{z_{0.95}^2}{4t_B^2} + \frac{C_{BA}}{t_B}\left(\frac{1}{t_S} + \frac{1}{t_B}\right) + \xi_{BA}^2} \quad (15)$$

$$x_C = \frac{S_C}{\varepsilon \times V_A \times Y \times D_A \times P_A} \quad (16)$$

where

S_C is the critical net count rate,
x_C is the critical massic or volumic activity,
$z_{0.95}$ is 1.645, the 95th percentile of the standard normal distribution, and

where all other symbols are as defined above. These critical values are calculated for each analysis and analyte. A detection decision for each analyte may be made by comparing the analyte's net count rate to S_C or by comparing its activity x to x_C

12.5 Use the following equation to calculate the minimum detectable activity (volumic or massic activity) for each analyte.

$$x_D = \frac{\frac{z_{0.95}^2}{2t_S} + S_C + z_{0.95}\sqrt{\frac{z_{0.95}^2}{4t_S^2} + S_C\left(\frac{1}{t_S} + \frac{z_{0.95}^2\varphi_S^2}{t_B}\right) + R_{BA}\left(\frac{1}{t_S} + \frac{1}{t_B}\right) + \xi_{BA}^2}}{\varepsilon \times V_A \times Y \times D_A \times P_A \times (1 - z_{0.95}^2\varphi_S^2)} \quad (17)$$

where

x_D is the minimum detectable activity,
R_{BA} is the background count rate in the analyte ROI,
S_C is an estimate of the critical net count rate calculated using equation 15 with $C_{BA} = R_{BA}t_B$, and
$z_{0.95}$ is 1.645, the 95th percentile of the standard normal distribution

13.0 DATA REVIEW

13.1 General Procedure:

13.1.1 See *NAREL Standard Operating Procedure for Review of Radiochemistry Data* (DR/SOP-2) for general procedures for data review.

13.1.2 The alpha-spectrometry system administrator or another person designated by the Nuclear Counting Laboratory Manager performs the first official review of actinide analysis results. However, the instrument operator should double-check his or her data entry for each analysis even if he or she is not the designated first reviewer.

13.1.3 If the spectrum is smeared, a recount should be requested of the counting room personnel. If upon recounting the spectrum is still smeared, the samples can be leached and coprecipitated again.

13.1.4 If unknown peaks are in the spectrum, the peaks must be identified by the energy level. If the peaks are breakthrough because of high concentrations, the sample should be reanalyzed using a smaller amount of sample or more appropriate reagents.

13.2 Actinide Data Review:

13.2.1 The first reviewer checks the spectrum from each actinide analysis and judges the reasonableness of the results. These checks are based on the report and spectrum graph printed by commercial analysis software. The reviewer must note on the printout whenever one or more ROIs have been manually adjusted.

13.2.2 The reviewer checks the data entry for each analysis by comparing the values printed on the report to the values written by the analyst on the assay batch form. He or she also checks that the source was placed at an appropriate shelf height in the alpha spectrometer and that the shelf height has been recorded correctly.

13.2.3 The reviewer checks that each peak present in the spectrum is at the expected location within its ROI, and that peaks do not spill over significantly from one ROI into another.

13.2.4 The reviewer checks that the background level for each ROI is below its pre-determined upper bound. Any ROI background that exceeds 60 counts in 3000 minutes is unacceptable. An even lower limit of 20 counts in 3000 min has been established for the ^{238}Pu, ^{239}Pu, and ^{241}Am ROIs.

13.2.5 The reviewer checks that the calibration for the recorded shelf height has not expired.

13.2.6 The reviewer checks that the chemical yield of the analysis meets the criteria described in the *NAREL Radiochemistry Quality Assurance Manual* (QA/QAM-1). If the yield does not meet the stated criteria, the reviewer must disapprove the analysis for reporting. See the *NAREL Standard Operating Procedure for Review of Radiochemistry Data* (DR/SOP-2) for further instructions in this case.

13.2.7 The reviewer checks that the net activity for each analyte is not less than zero by an amount that is statistically significant at the 1 % level. If a result is less than zero by a statistically significant amount, the reviewer must qualify the result as "rejected." See the *NAREL Standard Operating Procedure for Review of Radiochemistry Data* (DR/SOP-2) for further instructions in this case.

13.2.8 The reviewer checks that the FWHM for any peak with adequate counting statistics does not exceed 100 keV. This check is performed whenever the net count for the peak is greater than three times its associated standard uncertainty.

13.2.9 The reviewer completes the review when he or she runs Alpha-Review, an in house software system. The reviewer uses Alpha-Review to calculate results of actinide analyses and store them in the LIMS database. Alpha-Review automatically performs the objective tests described in paragraphs 13.2.4 - 8 and generates warnings for each failed test. The program also generates a printout for each completed analysis, showing raw data and results, any automatically generated warning messages, comments by the data reviewer, and the disposition selected by the reviewer (either approval or disapproval).

13.2.10 When the data review is complete, the Nuclear Counting Laboratory returns the assay batch form, the printouts from the commercial analysis software and Alpha-Review, and any other data sheets to the analyst. The reviewer initials and dates the printouts from the analysis software and Alpha-Review. The Alpha-Review printout indicates whether the reviewer approved or disapproved the results for reporting. When results are disapproved, the program requires the reviewer to provide the reason or reasons in the form of a comment, which is shown on the software printout.

13.2.11 The analyst double-checks the data entry performed by the Nuclear Counting Laboratory (NCL). This includes the sample number, aliquant size and units, tracer identification number, tracer reference date, tracer concentration, and amount of tracer used. The detector efficiency and matching shelf height will be compared to the list of detector efficiencies provided by the NCL. The analyst must also review the spectrum, results, yield, and count time and note any abnormalities. If abnormalities are recognized they should be discussed with the NCL personnel. Once the data has been reviewed appropriately, the analyst will initial and date the printouts from the analysis software, indicating agreement or disagreement with the judgment of the first reviewer.

13.2.12 The RDC performs an independent final review of the results after they have been stored in the LIMS and the analyst has submitted all documentation. The RDC also initials and dates the software printouts and indicates agreement or disagreement with the judgment of the first reviewer. Differences of opinion must be resolved before the results may be reported.

13.3 Americium:

13.3.1 Since the alpha-particle energies for ^{241}Am and ^{243}Am are not widely separated, the reviewer examines each americium spectrum carefully for spillover from one ROI into another.

13.3.2 Americium sources should never be analyzed on the topmost shelf in the spectrometer, because proximity to the detector tends to degrade peak resolution. The reviewer checks that the selected shelf height is appropriate for an americium source.

13.4 Plutonium:

13.4.1 Plutonium-238 is seldom found in environmental media at levels that are detectable by this method. NAREL commonly performs a confirmatory analysis for plutonium whenever the measured result for ^{238}Pu exceeds its estimated 3-sigma uncertainty.

13.4.2 If the ^{238}Pu activity in an unspiked sample is greater than its estimated 3-sigma expanded uncertainty, the reviewer must report the measured value to the Nuclear Counting Laboratory Team Leader and the RDC, and, if the sample is from the RadNet network, the reviewer must submit a RadNet Event Report.

13.5 Thorium:

13.5.1 In most solid samples, ^{232}Th and ^{228}Th occur in approximate equilibrium.

13.5.2 Since a thorium analysis requires more data entry than other alpha-particle spectrometry analyses, the RDC should double-check the data entry of all dates and tracer values for thorium analyses.

13.6 Uranium:

13.6.1 In most solid samples, ^{234}U and ^{238}U should exist in approximate radioactive equilibrium. In naturally occurring uranium, the ^{235}U activity should be about 5 % of the activity of ^{234}U or ^{238}U.

13.6.2 In water samples ^{234}U and ^{238}U may not be in equilibrium, but the ^{235}U activity should still be much less than the activity of either ^{234}U or ^{238}U.

13.6.3 If unusual ratios of uranium isotopes are measured, the reviewer should investigate and report the results to the Nuclear Counting Laboratory Team Leader.

14.0 METHOD PERFORMANCE

14.1 Method performance was evaluated in accordance with *NAREL Standard Operating Procedure for Initial Evaluation of an Analytical Method* (QA/SOP-3).

14.2 Each year, analysts analyze performance test samples as a measure of continual monitoring of method performance. Results are on file with the NAREL QA Manager.

14.3 Performance testing sample data:

14.3.1 Total Uranium – all water samples:

	Ref Date	Rpt. 1	Rpt 2	Rpt 3	True Value	%R
ERA-Rad 52	02/17/03	51.47	50.72	52.42	53.70	96
ERA-Rad 53	05/19/03	14.21	15.51	14.48	15.10	98
EML	03/01/04	4.29	4.34	4.23	4.62	93
ERA Rad-58	08/17/04	5.58	5.3	6.71	6.20	95
ERA-RAD-56	2/17/04	33.26	30.77	32.52	33.00	98
ERA Rad-62	08/16/05	4.29	4.58	4.2	4.45	98
ERA Rad-65	4/10/06	69.3	66.8	65.5	69.10	97
ERA Rad-66	7/10/06	40.5	39.4	40.1	40.30	99

14.3.2 Thorium-230 – all water samples:

Ref Date		Rpt Value	True Value	%R
04/01/04	Th-230	2.4	2.76	87
03/11/05	Th-230	2.269	2.44	93
03/11/05	Th-230	7.025	6.51	108
03/11/05	Th-230	2.404	2.44	99
04/01/05	Th-230	1.619	1.73	94
04/01/06	Th-230	1.7762	1.95	91

14.3.3 Americium-241 – all water samples:

Ref Date	Rpt. 1	Rpt 2	Rpt 3	True Value	%R
09/01/03	8.39	8.27	8.55	8.760	96
11/01/03	0.017			0.014	118
12/01/03	0.462	0.593	0.6	0.578	95
03/01/04	1.265	1.297	1.179	1.310	95
04/01/04	1.42			1.530	93
04/01/04	2.04			2.216	92

Ref Date	Rpt. 1	Rpt 2	Rpt 3	True Value	%R
03/11/05	1.078			1.018	106
03/11/05	1.098			1.018	108
1/1/2006	1.26			1.300	97
04/01/06	1.5524			1.560	100
07/01/06	2.2			2.310	95

14.3.4 Plutonium-238 – all water samples:

Ref date	Rpt. 1	Rpt 2	Rpt 3	True Value	%R
11/01/03	1.437			1.490	96
03/01/04	1.073	1.027	1.058	1.100	96
04/01/04	2.4			2.463	97
04/01/04	1.59			1.700	94
05/01/04	1.21			1.240	98
04/01/05	1.853			1.972	94
01/01/05	0.0185	0.0213	0.0229	0.018	116
04/01/05	1.399			1.531	91
01/01/06	0.936			1.000	94
04/01/06	1.5576			1.712	91

14.3.5 Plutonium-239/240 – all water samples:

Ref date	Rpt. 1	Rpt 2	Rpt 3	True Value	%R
03/11/05	2.612			2.660	98
01/01/05	2.526	2.514	2.46	2.400	104
11/01/03	2.157			2.390	90
07/01/06	1.76			1.940	91

15.0 POLLUTION PREVENTION

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA places pollution prevention as the management option of first choice.

15.2 Volumes of prepared reagents are made in the smallest amounts consistent with sample batch sizes to minimize having to discard unused reagents.

16.0 WASTE MANAGEMENT

16.1 The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. It is the responsibility of each laboratory to assure adherence to EPA regulations. Specific information can be found in the *NAREL Chemical Hygiene Plan.*

16.2 The waste stream generated from analyzing one sample for the previously described procedure is 25 mL of 12 M hydrochloric acid, 8 mL of 16 M nitric acid, 2 mL of 29 M hydrofluoric acid, 0.04 g of sodium nitrite, 0.19 g of oxalic acid, 2 g of aluminum nitrate, and 0.29 g of ammonium oxalate.

16.2.1 Acidic waste solutions are collected in a bucket, neutralized, and poured down the drain.

17.0 REFERENCES

17.1 Horwitz, E. Philip and Maxwell, Sherrod L., *Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste Solutions, Analytica Chemica Acta,* vol. 310, pp. 63-78, 1995.

17.2 Horwitz, E. Philip, *Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography, Analytica Chemica Acta,* vol. 281, pp.361-372, 1993.

17.3 Boll, R.A. and Schweitzer, G.K., *Sequential Separation Procedure for U, Th, Np, Pu, and Am*, University of Tennessee, Knoxville, TN, 1994.

17.4 *NAREL Standard Operating Procedure for Preparing Thorium-234 Tracer Solutions* (AMS/SOP-4).

17.5 *NAREL Standard Operating Procedure for Preparation of Self-Cleaning U-232 Tracer Solution* (AMS/SOP-6).

17.6 *NAREL Standard Operating Procedure for Preparing and Validating Radiochemical Tracers, Spiking Solutions, and Calibration Solutions* (QA/SOP-4).

17.7 *NAREL Chemical Hygiene Plan.*

17.8 *NAREL Radiation Safety Manual* (HS/M-1).

17.9 *NAREL Standard Operating Procedure for Calibration, Use, and Maintenance of Pipets* (SE/SOP-4).

17.10 *NAREL Standard Operating Procedure for Maintenance and Use of Balances* (SE/SOP-1).

17.11 *NAREL Standard Operating Procedure for Calibration and Use of Alpha Spectrometers Using AlphaVision* (NC/SOP-8).

17.12 *NAREL Standard Operating Procedure for Microwave Digestion of Samples for Actinide, Strontium, Radium, and Alpha/Beta Analyses* (AMS/SOP-7).

17.13 *NAREL Standard Operating Procedure for Initial Evaluation of an Analytical Method* (QA/SOP-3).

17.14 *NAREL Radiochemistry Quality Assurance Manual* (QA/QAM-1).

17.15 *NAREL Standard Operating Procedure for Review of Radiochemistry Data* (DR/SOP-2).

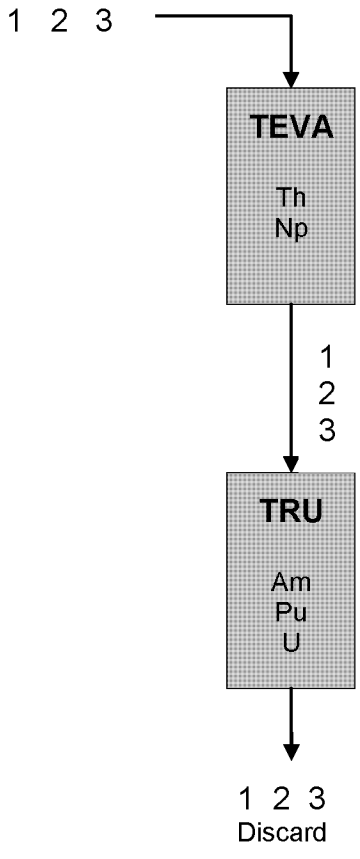
18.0 APPENDICES (TABLES, DIAGRAMS, AND FLOWCHARTS)

18.1 Actinides Separation Scheme – Part 1.

18.2 Actinides Separation Scheme – Parts 2 and 3.

Appendix 18.1

ACTINIDES SEPARATION SCHEME – Part 1



With cartridges in series:

1. Load solution:
   2.5 M HNO_3 / 0.5 M $Al(NO_3)_3$,
   ferrous sulfamate, ascorbic acid.
   Elements are loaded in the
   following valence states:
   - Am+3
   - Pu+3
   - Th+4
   - U+6
   - Np+4

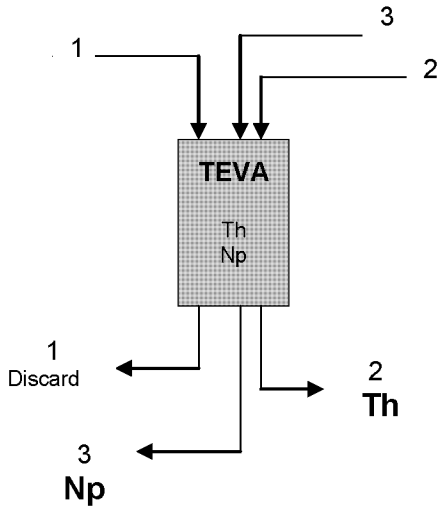
   Discard eluent.

2. Rinse with 2.5 M HNO_3, ferrous sulfamate. Discard eluent.

3. Rinse with 2.5 M HNO_3.
   Discard eluent.

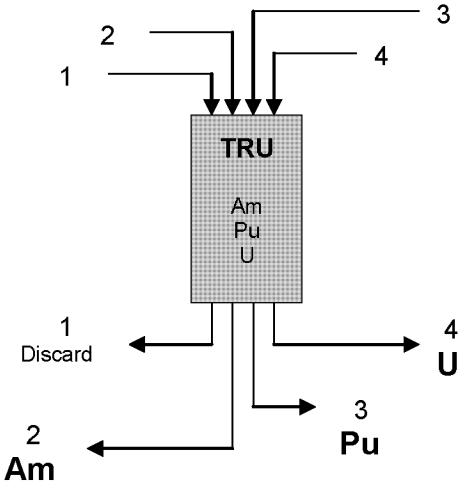
Appendix 18.2

ACTINIDES SEPARATION SCHEME – Parts 2 and 3



TEVA cartridge:

1. Rinse with 2.5 M HNO_3. Discard.
2. Elute thorium with 6 M HCl.
3. Elute neptunium with 0.1 M HCl / 0.5 M HF / 0.03 M TiCl.



TRU Cartridge:

1. Rinse with 2.5 M HNO_3.
   Oxidize Pu+3 to Pu+4 with 2.5 M HNO_3 / 0.1 M $NaNO_2$.
   Rinse with 2.5 M HNO_3.
2. Elute americium with 4 M HCl.
3. Elute plutonium with 0.1 M HCl / 0.1M $H_2C_2O_4$.
4. Elute uranium with 0.1 M $(NH_4)_2C_2O_4$.